

Nonlinear optical refraction of the dye-doped E7 thermotropic liquid crystal at the nematic-isotropic phase transition

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Abstract

It is known that the doping of liquid crystal with dyes usually changes the physical properties of the host, like the transition temperatures and the optical absorption among others. In this work we report a study of the nonlinear optical refraction of a dye doped sample of the E7 thermotropic liquid crystal by the Z-scan technique. It was found that the nonlinear refraction of the sample is higher than the undoped one, diverging at the clearing point. Close to the N-I transition, the nonlinear birefringence is characterized by a critical exponent that seems to confirm the tricritical hypothesis of the nature of the N-I phase transition, being independent of the doping.

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I. INTRODUCTION

In the field of liquid crystals, the Nematic-Isotropic (N-I) phase transition is the most studied phenomenon, both theoretically and experimentally, due to puzzling facts about its nature. Although initially it was suggested that the N-I transition should be of first order[2, 3], new experimental data show that it can be of a tricritical character[1, 4–10]. Recently we reported on the nonlinear optical properties of the E7 liquid crystal at the N-I phase transition where it was shown that close to the clearing temperature, the nonlinear birefringence diverges following an exponential law with an exponent that seems to support the tricritical hypothesis[11].

The doping of liquid crystals with dyes usually leads to changes in the optical properties of the host. There have been reported not only changes in the optical absorption but also changes in the order parameter and transition temperatures [12], the optical Fréedericksz transition threshold[13] and the nonlinear optical properties[14–16], being dependent on the characteristics of the dyes. In a previous work, the doping of the comercial liquid crystal E7 with a rod-like fluorescent dye (4,7-Bis(2-(4-(4-decylpiperazin-1-yl)phenyl)ethynyl)- [2,1,3]-benzothiadiazole) was investigated and the optical properties characterized [17]. The aligned liquid crystal host induced the ordering of the dye molecules, resulting in highly polarized light emission.

The main purpose of this article is to report on the nonlinear optical refraction of the E7 liquid crystal in the neighborhood of the N-I phase transition under the addition of the [2,1,3]-benzothiadiazole dye, employing the Z-scan technique. This report is organized as follows: in section two we describe the samples and the Z-scan technique. In section 3 we present the experimental results and the discussions. Finally, in section 4, we withdraw the conclusions.

II. EXPERIMENTAL DETAILS

The abbreviation E7 stands for a liquid crystal mixture consisting of several types of cyanobiphenyls, mainly 5CB, and in less quantity triphenyls. It exhibits a nematic phase in the temperature interval from -10°C till the transition to the isotropic phase at $T_{NI} = 58.1^\circ\text{C}$. In this work we used comercial E7 (Merck) without further purification. The synthesis and optical properties of the [2,1,3]-benzothiadiazole dye were published elsewhere [17, 18]. The dye-doped liquid crystal samples were prepared with three different molar concentrations of dye: 0.025%w, 0.075%w and 0.2%w, labeled S1, S2 and S3 for shortness, respectively. A fourth sample without doping was used for comparison (labeled S0). Samples were conditioned in parallel glass cells, separated by $20\text{ }\mu\text{m}$ thick spacers. The glass plates were coated with PVA (polyvinyl alcohol) and buffed for homogeneous planar alignment of the liquid crystal. The sample was placed in a hot stage (Instec) with a computer-controlled translational stage (Newport). The temperature of the samples were controlled with a precision of 0.2°C between 20°C and the T_{NI} . The clearing temperature of the mixed system liquid crystal+dye depends on the percentage of the dye. The T_{NI} transition temperatures of the samples S0, S1, S2 and S3 were measured by optical polarized light microscopcy using a temperature controlled hot stage (Instec) where the values of 58.1°C , 59.0°C , 59.4°C and 60.1°C , respectively, were obtained.

The Z-scan technique exploits the formation of a lens in a medium by a focused Gaussian-profile laser beam, measuring the transmitted intensity of the sample as a function of position along the direction of propagation of the beam (the z -axis)[19]. The magnitude and sign of the nonlinear refraction n_2 can be obtained by means of the closed-aperture Z-scan technique (Fig. 1). In the closed-aperture setup the transmitted intensity is measured behind an iris centered along the z -axis. A medium characterized by a $n_2 > 0$ ($n_2 < 0$) behaves like a positive (negative) lens. The transmittance of the sample at the z position, normalized by the transmittance of the sample at a far position of the focus of the lens ($z \rightarrow \infty$), in the closed-aperture (Γ_c) configuration of the Z-scan technique is given by Eq. (1) [19, 20]. This is the case for systems that exhibit both nonlinear refraction and nonlinear absorption, with the assumptions of local cubic nonlinearity, sufficiently thin sample and to first-order corrections in the irradiance of a Gaussian laser beam at the far field condition.

$$\Gamma_c = 1 - \frac{4\Phi\left(\frac{z}{z_o}\right)}{\left[1 + \left(\frac{z}{z_o}\right)^2\right]\left[9 + \left(\frac{z}{z_o}\right)^2\right]} - \frac{\Theta\left[\left(3 + \left(\frac{z}{z_o}\right)^2\right)\right]}{\left[1 + \left(\frac{z}{z_o}\right)^2\right]\left[9 + \left(\frac{z}{z_o}\right)^2\right]}. \quad (1)$$

where z_o is the Rayleigh range of the beam, $\Phi = k n_2 I_o L_{ef}$, k is the wave number, $L_{ef} = [1 - \exp(-\alpha_o L)] / \alpha_o$ is the effective thickness of the sample, I_o is the irradiance at the beam waist of the laser, α_o is the linear optical absorption and Θ is proportional to the nonlinear absorption. However under incidence of a moderated-power cw laser beam, the nonlinearity in a nematic liquid crystals is essentially from thermal origin due to the temperature dependence of the order parameter S . It is said that the laser induce a Thermal Lens and the intensity of this effect is proportional to the thermo-optical coefficient dn/dT [21], i.e. the refraction index can be written as $n = n_0 + (dn/dT) \Delta T$, where ΔT

is the change in temperature [22]. Although the diffusion of heat leads to a phase variation of the laser beam which does not match exactly its intensity spatial profile, for samples with low absorption and low thermal conductivity, it was shown [23] that the Shake-Bahae's model for the Z-scan experiment, based in a purely local effect, gives a good description of the transmittance. In this case, it is possible to write that $dn/dT \propto n_2$, where n_2 and dn/dT are the fitting parameters of the Sheik-Bahae model [19] and the Thermal Lens model, respectively.

Our experimental setup uses a cw laser ($\lambda = 532\text{ nm}$, Ventus, Laser Quantum) with power in the range of 3 – 40 mW. The beam waist at focus was about $26\text{ }\mu\text{m}$, and data acquisition was made *via* oscilloscope (Tektronix). The polarization of the laser beam (\mathbf{E}) was set either parallel or perpendicular to the nematic director (\mathbf{n}) induced by the surface treatment, therefore, reorientation of the nematic director by an optical torque ($\mathbf{\Gamma}_{\text{opt}} = \mathbf{D} \times \mathbf{E}$) is not expected to occur.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Fig. 2 shows the typical closed-aperture Z-scan trace, obtained with sample S2 at $T = 25^\circ\text{C}$ (nematic phase) for $\mathbf{n} \parallel \mathbf{E}$. The error bars correspond to the standard error of the mean value for at least ten measurements in each z -position. As can be seen, for $\mathbf{n} \parallel \mathbf{E}$ the sample exhibits the valley-peak configuration corresponding to a negative nonlinear refraction coefficient ($n_{2\parallel} < 0$). On the other hand, for $\mathbf{n} \perp \mathbf{E}$ the samples exhibit positive nonlinear refraction ($n_{2\perp} > 0$) (figure not shown). These results are consistent with the laser heating of the sample. An increase of temperature leads to a wider angular distribution of the long molecular axis around the nematic director. So, the effective molecule seen by the laser beam is shorter along the molecular axis and thicker in a perpendicular direction, resulting in a diminution of the extraordinary refraction index and an increase of the ordinary refraction index, respectively. We have also checked the nonlinear optical response of the empty glass cell with PVA coating: for the intensities of the laser beam used in our experiment, the cell does not show any nonlinear optical response.

Fig. 3 shows the nonlinear refraction of the samples in the nematic and in the isotropic phases for both relative orientations between the nematic director and the polarization of the laser as a function of the normalized temperature T/T_{NI} . For $\mathbf{n} \parallel \mathbf{E}$ (filled symbols) the samples display a self-defocusing effect ($n_{2\parallel} < 0$) and for $\mathbf{n} \perp \mathbf{E}$ (empty symbols) the samples display a self-focusing effect ($n_{2\perp} > 0$) in the full nematic region. Approaching T_{NI} from below, the modulus of n_2 diverges for both relative orientations between the polarization of the optical beam and the nematic director. Fig 4 shows the nonlinear birefringences $\Delta n_2 = n_{2\parallel} - n_{2\perp}$ of the samples as a function of temperature. As observed, the magnitude of the nonlinear birefringence increases as T_{NI} is approached from below. Although in the nematic phase far from T_{NI} the birefringence of all the samples are rather similar, close to T_{NI} the higher the doping of dye, the bigger is the birefringence. As the dye absorption is dominant over the liquid crystal E7 at 532 nm, the nonlinear response measured here comes mainly from the dyes, and that explains the nonlinear birefringence behavior with the dye concentration. It was shown [11] that in the nematic phase and close to the clearing point the nonlinear birefringence can be written as

$$\Delta n_2 \propto \left[1 - \frac{T}{T^\dagger} \right]^{\beta-1}, \quad (2)$$

where β is the effective critical exponent associated with the order parameter and T^\dagger , the temperature of the virtual second order transition seeing from below T_{NI} , represents the absolute limit of the nematic phase on heating. For the homologous series of cyano-biphenyls $n\text{CB}$, with $n=5$ to 8, $T^\dagger - T_{NI} \simeq 0.2^\circ\text{C}$ [7], being of the order of the uncertainty of our measurement of temperature. Figure 5 shows a $\ln\text{-}\ln$ plot of $|\Delta n_2|$ as a function of the reduced temperature $1 - \frac{T}{T^\dagger}$ for sample S3 supposing $T^\dagger = T_{NI}$. Similar plots were obtained for the other samples. To perform the best fitting we proceeded to vary T^\dagger at regular steps in the temperature range $[T_{NI}, T_{NI} + 0.4^\circ\text{C}]$ for each sample and the weighted averages of the effective critical exponents β are summarized in Table 1.

The value of β is rather independent of the dye doping concentration, but is a little higher for the pure E7 sample, nevertheless they also support the tricritical hypothesis of the N-I phase transition. It is important to emphasize that the exponents β obtained for the doped samples (S1, S2 and S3) are mainly associated to the dye order parameter. From previous work [17] we observed that the dye order parameter increases in the range of concentration investigated here, so it is possible to conclude that the critical exponent β is not directly affected by changes in the molecular order parameter.

IV. CONCLUSIONS

To summarize, it was investigated the nonlinear optical properties and the nonlinear refraction of the dye-doped E7 liquid crystal in the nematic phase, close to the N-I transition under continuous 532-nm wave excitation by the Z-scan technique. The nonlinear optical refraction exhibit opposite character for the two geometrical configurations of the nematic director relative to the polarization of the incident beam, being $n_{2\parallel} < 0$ and $n_{2\perp} > 0$, in all the nematic phase. Approaching the clearing point from below, the nonlinear refraction diverges. The effect of the dye is to amplify the behavior observed in the undoped sample. Curiously, the amplification of the nonlinear response is higher for $\mathbf{n} \perp \mathbf{E}$ than for $\mathbf{n} \parallel \mathbf{E}$. The nonlinear birefringence is characterized by a critical exponent that seems to confirm the tricritical hypothesis of the N-I phase transition which predicts a value 0.25. The tricritical character of the N-I phase transition seems to be independent of the E7 liquid crystal doping.

Acknowledgments

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Figure Captions

Fig. 1: Sketch of the apparatus for the implementation of the closed-aperture Z-scan: L (lens), S (sample), I (iris), and PD (photodetector).

Fig. 2: Typical Z-scan curve obtained for $\mathbf{n} \parallel \mathbf{E}$ with closed-aperture configuration Z-scan technique ($T = 25^\circ\text{C}$). The solid line shows the fitting to Eq. 1.

Fig 3: Nonlinear refraction as a function of temperature in the nematic and isotropic phases, for both configurations between the nematic director and the polarization of the incident beam: $\mathbf{n} \parallel \mathbf{E}$ (full symbols) and $\mathbf{n} \perp \mathbf{E}$ (empty symbols).

Fig. 4: Nonlinear birefringence Δn_2 of the samples as a function of temperature. Vertical dashed line indicates T_{NI} .

Fig. 5: $\ln\text{-}\ln$ plot of the absolute value of Δn_2 as a function of the reduced temperature $1 - T/T_{NI}$. Solid line represents a typical linear fitting of data.

Table Captions

Table 1: Values of the effective critical exponents β associated to the order parameter for the doped (S1, S2, S3) and the undoped (S0) samples measured from the nonlinear birefringence Δn_2 at the N-I phase transition.

Table	
Sample	β
S0	0.28 ± 0.03
S1	0.22 ± 0.04
S2	0.23 ± 0.03
S3	0.21 ± 0.03

Fig. 1

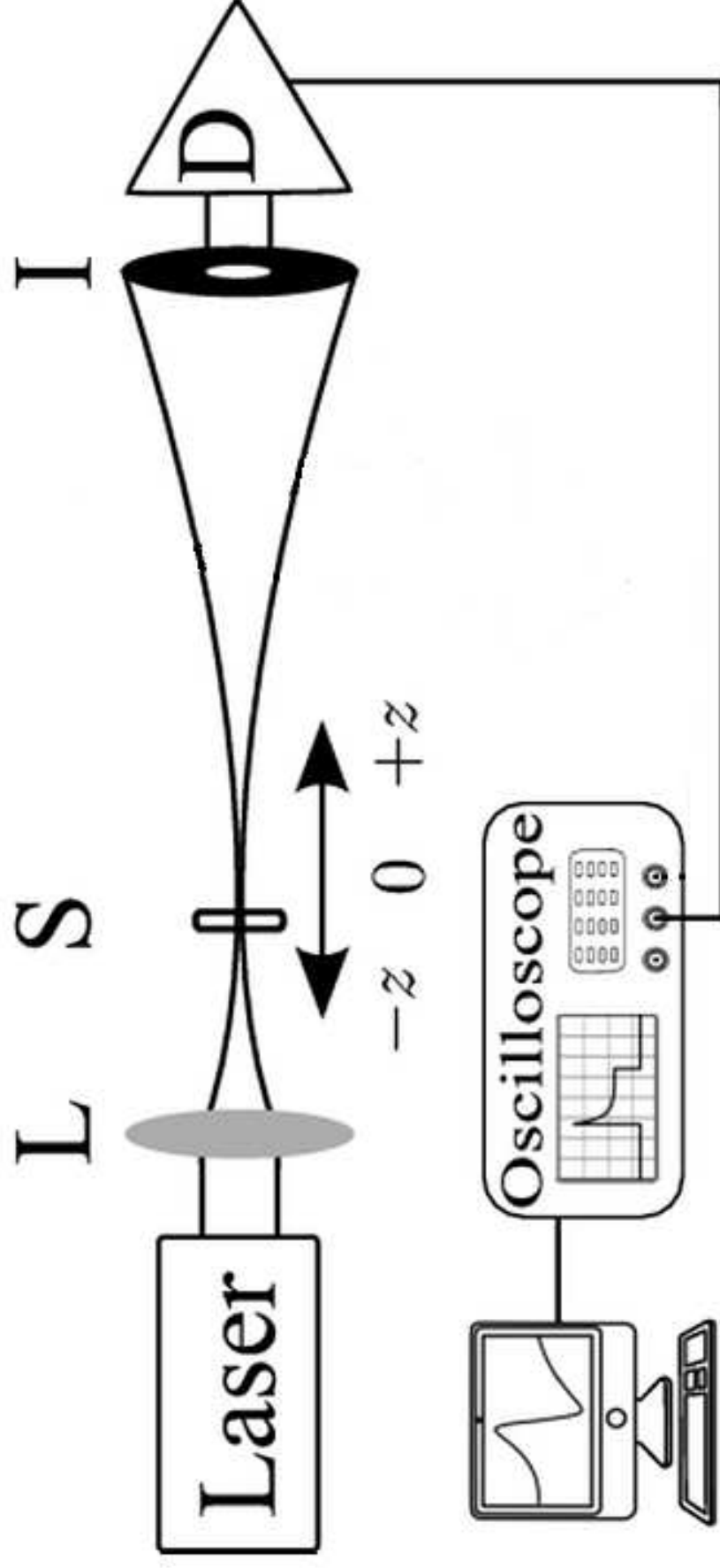


Fig. 2

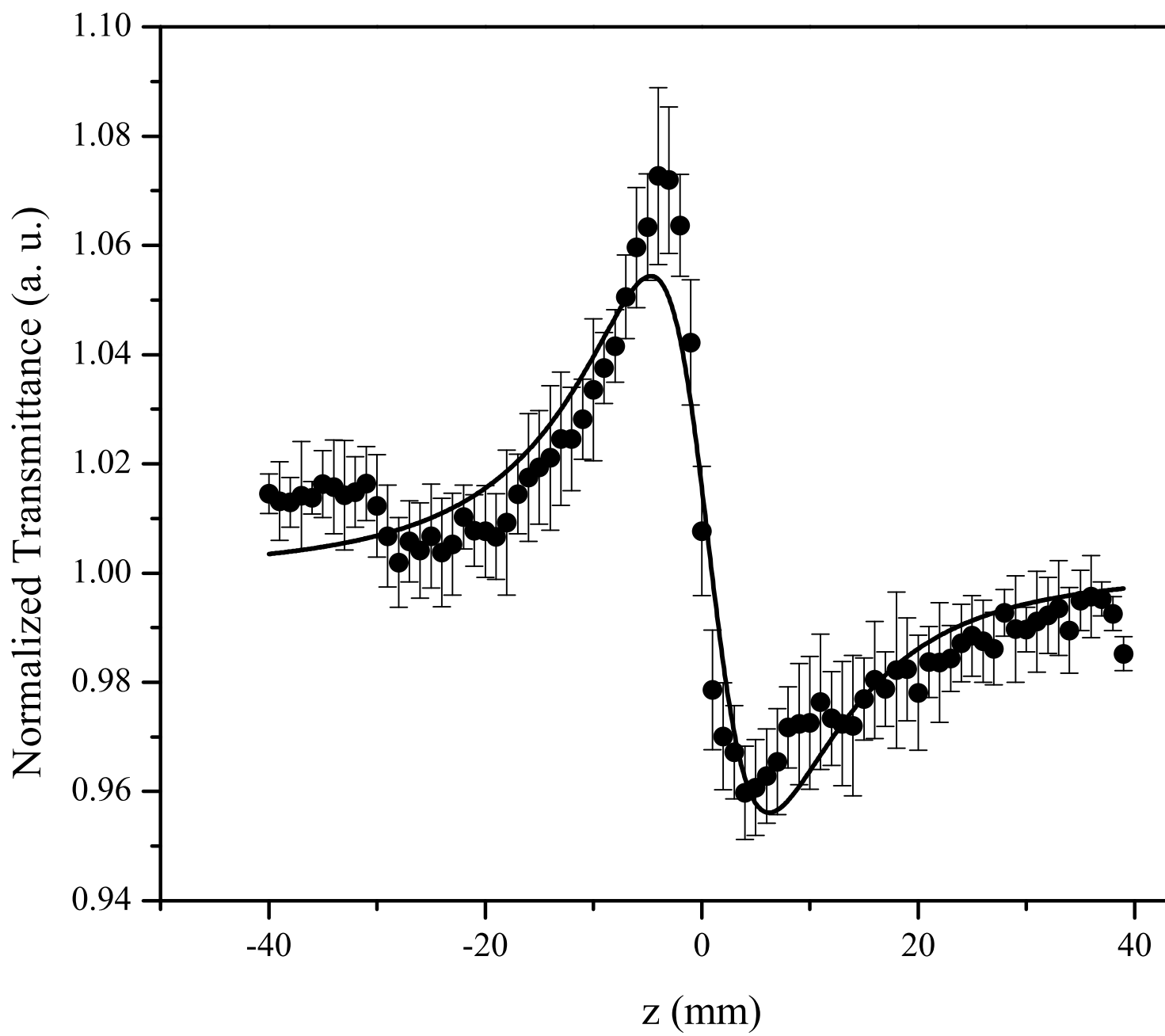


Fig 3

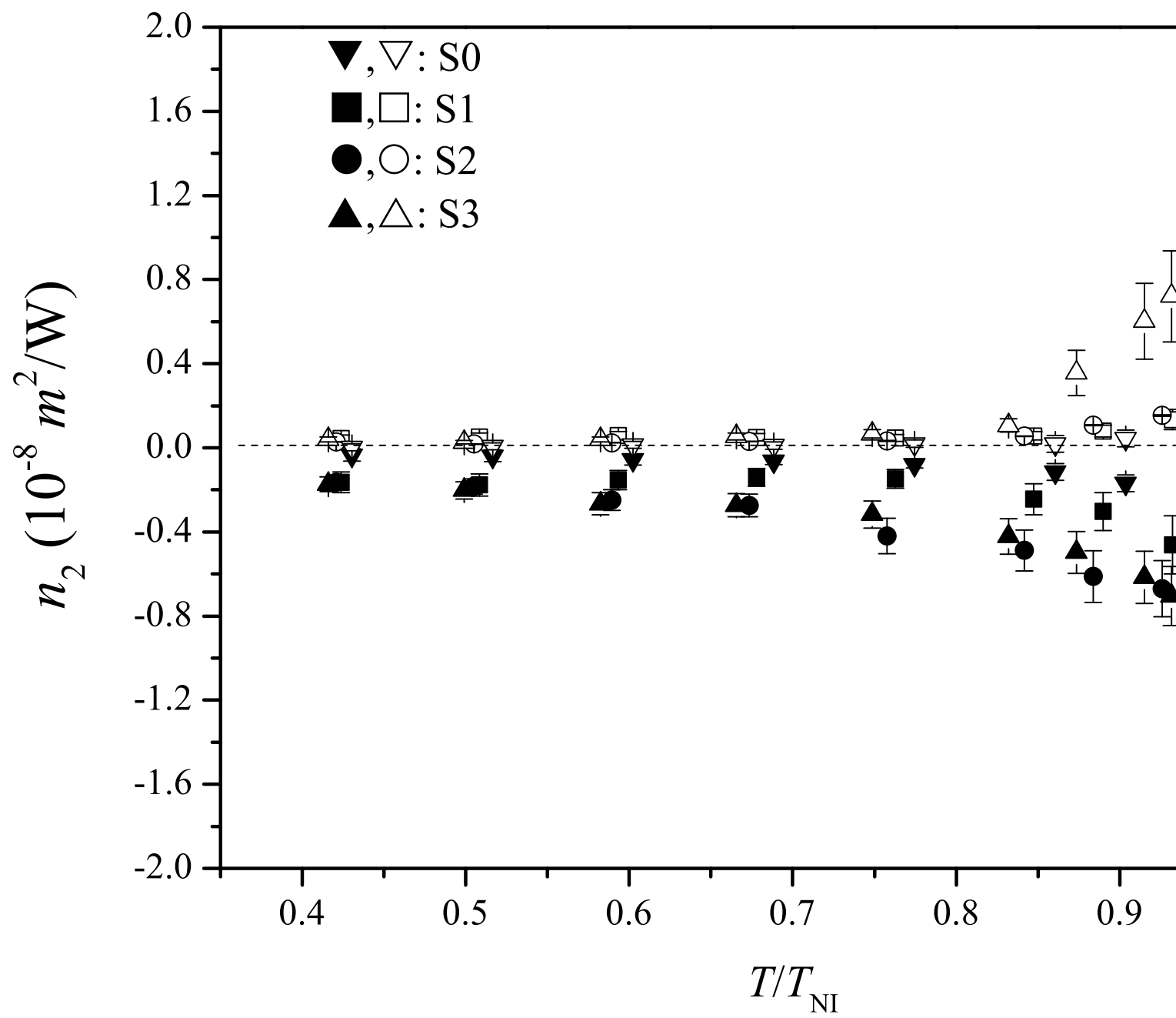


Fig 4

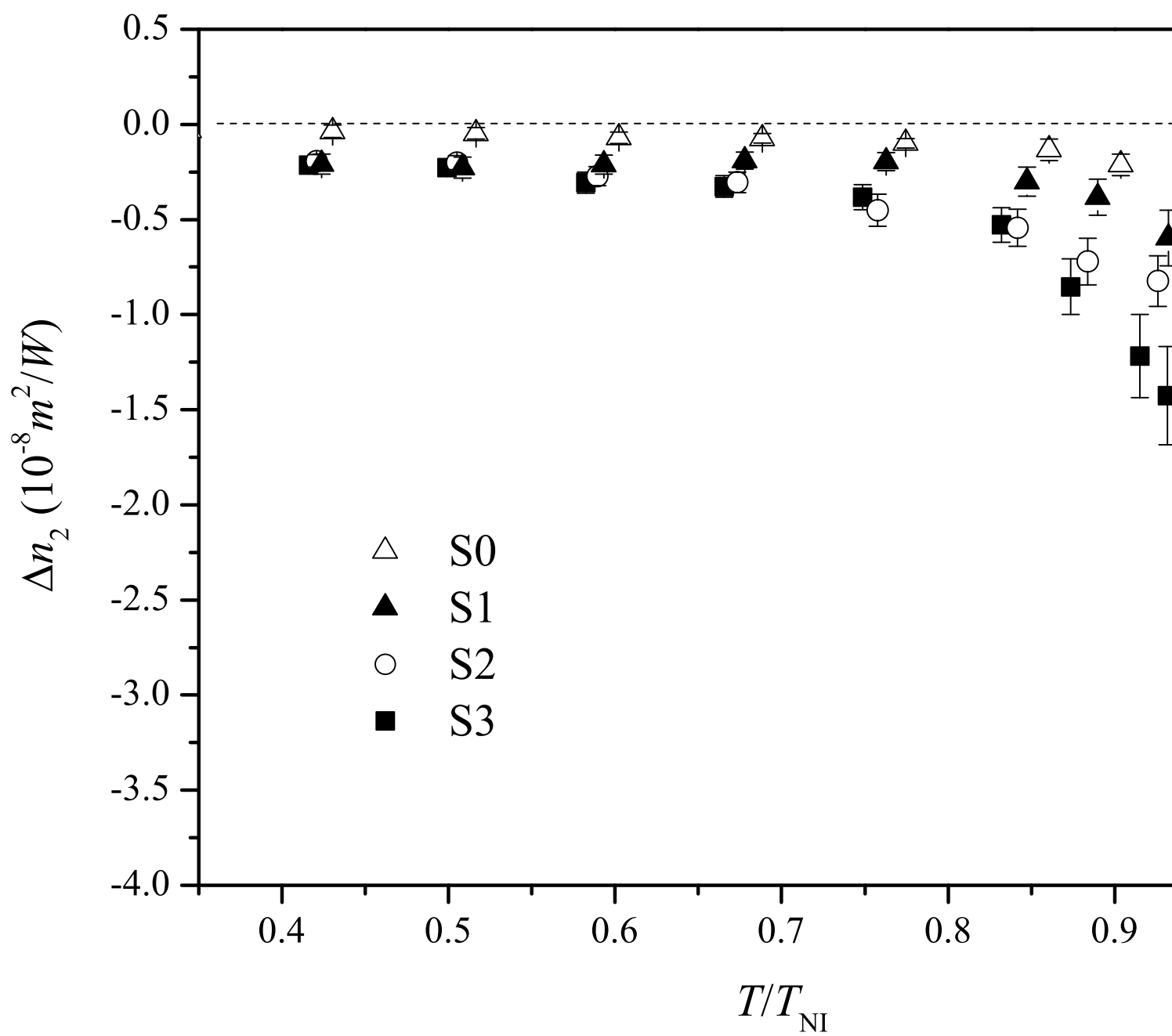


Fig 5

